

TOPIC E – ENVIRO CHEMISTRY PART 9 – FURTHER OZONE FOR HL

IB Chemistry

Topic E – Enviro

Hodder Ed - Talbot



E9 Ozone depletion - 1 hour

- E.9.1 Explain the dependence of O₂ and O₃ dissociation on the wavelength of light. (3)
- E.9.2 Describe the mechanism in the catalysis of O₃ depletion by CFCs and NO_x. (2)
- E.9.3 Outline the reasons for greater ozone depletion in polar regions. (2)



E9.1 – Wavelength and Frequency

- E.9.1 Explain the dependence of O₂ and O₃ dissociation on the wavelength of light. (3)
 - $\lambda = 242 \text{ nm}$ $O_2 \rightarrow 2O\bullet$
 - $\lambda = 330 \text{ nm}$ $O_3 \rightarrow O_2 + O\bullet$
 - *The energy needed should be related to the bonding in O₂ and O₃.*
- Specific wavelengths of UV radiation are absorbed by specific reactions in the stratosphere.
- The wavelength(λ) and frequency(f) are related in the wave equation formula:

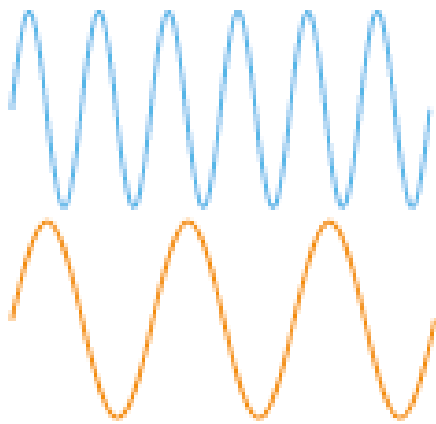


Speed of light in a vacuum (const) = freq (f) x WL (λ)

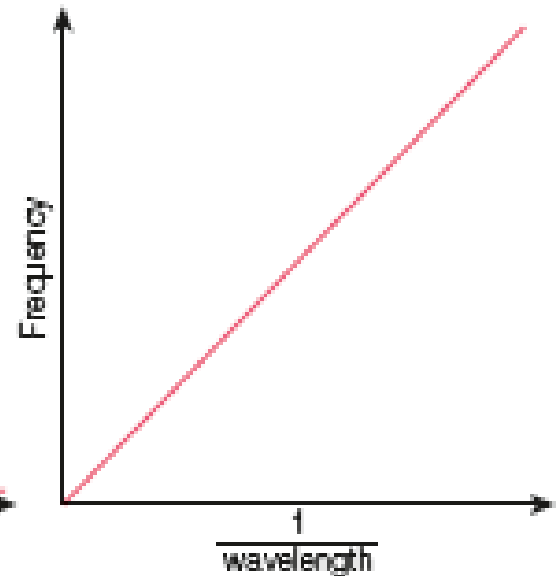
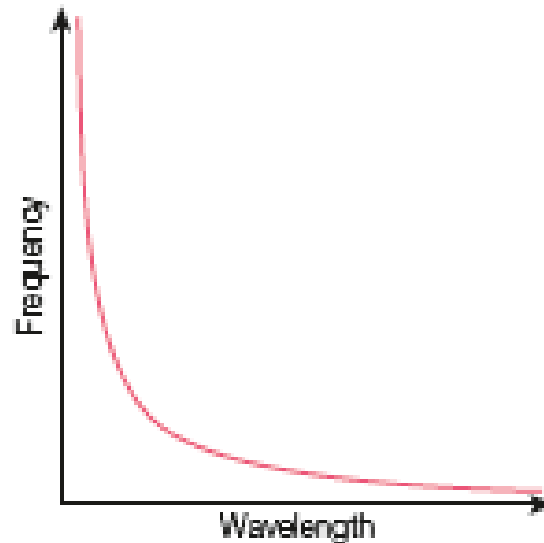
$$c = f \times \lambda$$

E9.1 – Inverse Relationship

- Since the speed of light is constant:
 - Increasing f means a decreasing λ
 - UV-c radiation, with $\lambda = (200-288)\text{nm}$ has higher frequency than UV-b radiation, with $\lambda = (280-320)\text{nm}$



same speed
different wavelength
different frequency



E9.1 – Energy to break bonds

- The frequency of radiation correlates with its energy, according to the formula:
 - $E = h \times f$, where h represents Planck's constant
 - Shorter λ = higher f electromagnetic radiation therefore has a higher energy than the longer λ , lower f electromagnetic radiation
 - As we know from Part 04, the equations for ozone production and depletion are:

- ◆ $\lambda < 242\text{nm}$ (UV-c)



- ◆ $\lambda = 290\text{-}320\text{nm}$ (UV-b)

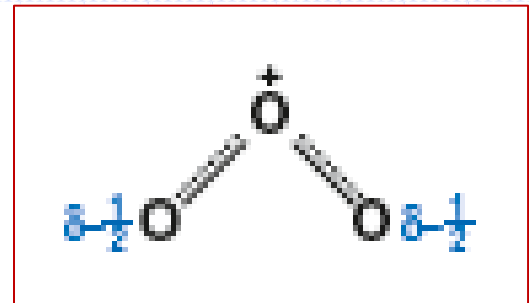
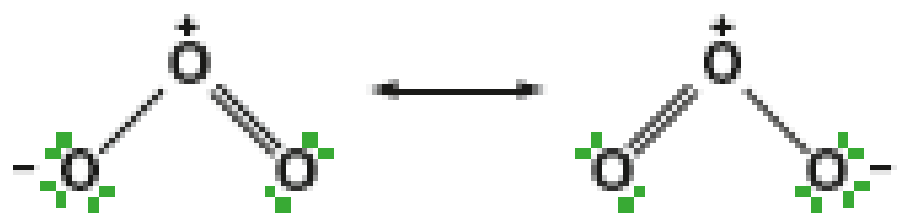


λ is shorter and it therefore takes more energy (high f) to break the $\text{O}=\text{O}$ than in O_3 where it can have resonance of a $\text{O}-\text{O}$ bond



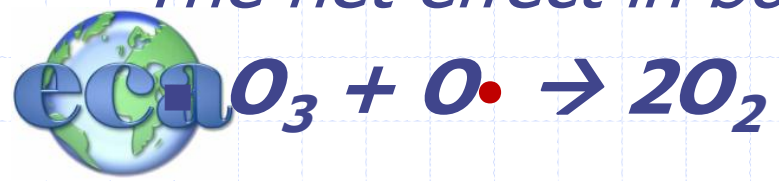
E9.1 – Resonance of Ozone

- $\text{O}=\text{O}$ $\Delta H_f = 498$ —
- $\text{O}-\text{O}$ $\Delta H_f = 144$ —
- The O_3 molecule contains resonance and the overall bonds are considered intermediate between single and double bonds so
 - In O_3 for the $\text{O}-\text{O}$ bonds, $\Delta H_f = 445$ —



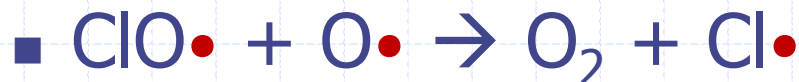
E9.2 – Mechanism for O₃ depletion

- E.9.2 Describe the mechanism in the catalysis of O₃ depletion by CFCs and NO_x. (2) *For example:*
 - $CCl_2F_2 \rightarrow CClF_2 + Cl\bullet$
 - $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
 - $ClO\bullet + O\bullet \rightarrow O_2 + Cl\bullet$
- AND
 - $NO + O_3 \rightarrow NO_2 + O_2$
 - $NO_2 + O\bullet \rightarrow NO + O_2$
- The net effect in both is:



E9.2 – Chlorine Photodissociation

- Ozone depletion by CFC's involves the photodissociation of a CFC molecule by a photon,
 - $\text{CF}_2\text{Cl}_2 + \text{UV} \rightarrow \text{CF}_2\text{Cl}\bullet + \text{Cl}\bullet$ (photodissociation of CFC-12)
- The highly reactive chlorine atom (free radical) goes on to react with an ozone molecule. The chlorine atom can later regenerate by reaction with an oxygen atom:



This is a chain reaction. One photon initiates the formation of one chlorine atom, which can then destroy thousands of ozone molecules, as the chlorine is regenerated by collision with O_2 atoms, which are abundant in the stratosphere.



E9.2 – Chlorine Compounds

- Ozone is also depleted by reaction with the oxychlorine radicals, $\text{ClO}\cdot$, to form chlorine dioxide
 - $\text{ClO}\cdot + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$
- The Chlorine radical, $\text{Cl}\cdot$, will not continue to remove ozone indefinitely as the cycle is eventually broken by collisions with other species.
 - $\text{ClO}\cdot + \cdot\text{NO}_2 \rightarrow \text{ClONO}_2$
 - $\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot\text{CH}_3$
 - $\text{Cl}\cdot + \text{H}_2 \rightarrow \text{HCl} + \cdot\text{H}$

HCl and ClONO_2 are 'sink' compounds which temporarily 'lock-up' the $\text{Cl}\cdot$ and $\text{ClO}\cdot$ radicals. Atmospheric conditions can force release of these radicals. This is the basis of seasonal variation in ozone depletion



E9.2 – N₂O Ozone Depletion

- As discussed earlier (part 04) nitrogen monoxide, NO, is formed in the stratosphere by the reaction of nitrous oxide, N₂O, with an oxygen atom
 - $\text{N}_2\text{O} + \text{O}\bullet \rightarrow 2\text{NO}\bullet$
- Nitrogen monoxide can deplete ozone as follows:
 - $\bullet\text{NO} + \text{O}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$
 - $\text{NO}_2 + \text{O}\bullet \rightarrow \text{NO} + \text{O}_2$
- Again, the nitrogen monoxide has been regenerated and can continue depleting more ozone molecules.



E9.3 – Polar Ozone

- E.9.3 Outline the reasons for greater ozone depletion in polar regions. (2)
 - *Consider the seasonal variation in temperature in the upper atmosphere. Refer to surface catalysis on ice particles.*
- Most CFC's are released in the tropical and temperate regions, where most of the Earth's population live
- However, ozone layer damage has been confined to the polar regions

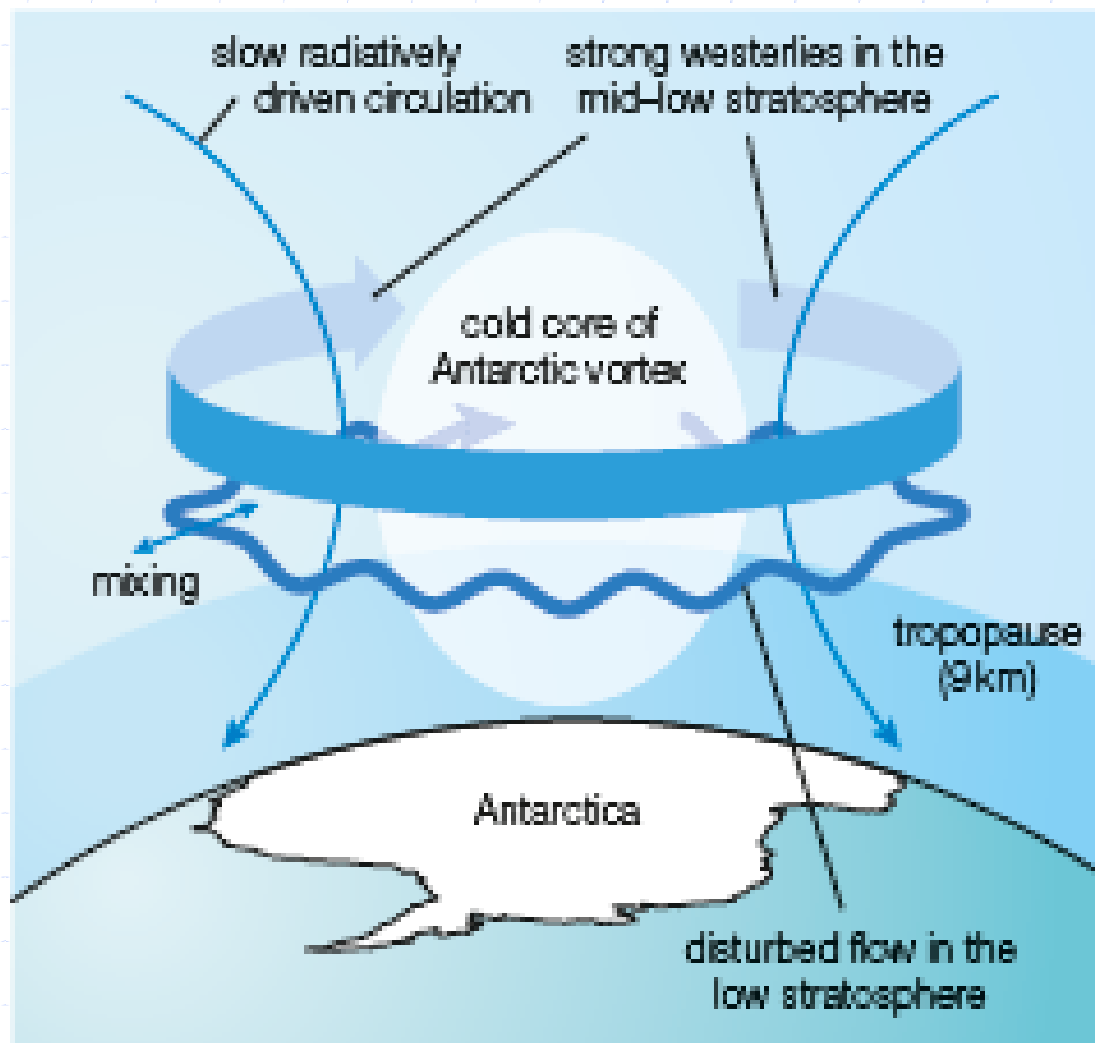


E9.3 – Polar Vortex

- Long-term studies of $[O_3]$ suggest that depletion is fastest in the spring months
 - September-October in the Antarctic
 - March-April in the Arctic
- The polar regions are naturally colder than the tropics, and in addition, air currents in the stratosphere tend to isolate a region of air above the poles so it does not mix with the tropical air during the polar winter.
 - This results in very low temperatures in the polar stratosphere, -80°C . This is termed the **polar vortex**



E9.3 – Polar Vortex



E9.3 – Polar Stratospheric Clouds

- These low temps result in high-altitude **polar stratospheric clouds** (PSC's)
 - H_2O and HNO_3 condense on pre-existing microparticles on sulfur (S) containing compounds. (at low T's form ice crystals)
 - The existence of these clouds (PSC's) along with the isolation of gas at the poles, a shift in the chlorine containing compounds occurs:
 - ◆ Instead of HCl and ClONO_2 , species such as Cl_2 appear
 - ◆ This occurs bc the cloud particles offer a catalytic surface which speeds up gas phase reactions and through the winter the PSC reactions build up Cl_2



E9.3 – Winter/Spring at Polar Latitudes

- Remember, ozone depletion is caused by UV radiation.
- In the winter, the extreme polar latitudes receive almost not sunlight so limited depletion
- In the spring, the Sun reappears and photolysis the **$\text{Cl}_2(\text{g})$** (favored chlorine containing compound) that have built up through the winter to form **$\text{Cl}\cdot$** , which enter the ozone depletion cycle and cause a **sudden rapid depletion of ozone**



E9.3 – Summer at Polar Latitudes

- In summer, the temperatures rise and the polar vortex is no longer in effect and the PSC's disperse
- The balance in chlorine compounds shifts back to more stable (unreactive) compounds.
- The ozone depletion stops and the hole has a chance to rebuild itself through photochemical reactions
 - The hole also is rebuilt by finally mixing with ozone-rich air from higher latitudes through the summer.



Compounds favored are **HCl** and **ClONO₂**